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(54) Coloured hot melt ink jet vehicle

(57) A coloured material suitable for use in a hot melt ink comprises a oligomeric hot melt ink jet vehicle formed of molecules having a backbone and at least one pendant side-chain. A dyestuff is reacted onto the backbone. The material is preferably obtainable as the reaction product of an aliphatic or aromatic mono- or di-isocyanate and a hydroxyl group functional dye component, and optionally one or more other suitable material. Such suitable materials include mono- and dihydric alcohols, primary and secondary monoamines, functional amides, hydroxyl functional amines and hydroxyl containing components having a terminal unsaturated bond.

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### HOT MELT INK JET VEHICLE

This invention is concerned with the formulation of hot melt ink jet base materials which are coloured.

Ink jet printing generally comprises forming a patterned array of droplets of an ink upon a substrate to form the desired indicia on the substrate. In a hot melt ink jet printing process, the ink is one which is normally solid at ambient temperatures and which is applied to the substrate in molten form so that the droplets solidify on cooling on the substrate.

Typically, the ink employed in hot melt ink jet printing comprises a fusible carrier together with a colourant, i.e. a pigment or dyestuff. Suitable materials for use as or in the vehicles for inks for hot melt ink jet printing (hereinafter, simply, "hot melt inks") should be relatively hard and non-tacky at ambient temperatures whilst being capable of melting to form mobile liquid inks. Suitably, they have a melting point of at least 65°C.

Patent Specification WO 94/14902 describes the use of certain urethane oligomers as hot melt ink vehicles. These oligomers are the reaction products of diisocyanates with a monohydric alcohol component, optionally followed by another monohydric component or a dihydric alcohol component followed by a monohydric alcohol component. These materials have melting points in excess of 65°C, low melt viscosities and good colour and viscosity stabilities at elevated temperatures. However they must be dyed by addition of a separate dyestuff in order to be used as ink jet inks.

Common problems which arise with the use of dyestuffs in ink jet inks are those of lightfastness and bleed. The former refers to the tendency of the dyes to fade in colour when exposed to long periods of UV radiation, eg. from sunlight. The latter refers to the tendency of

dyestuffs to leach from the ink into the substrate onto which the ink has been printed, giving a fuzzy image or causing the image to appear on the reverse of the substrate (also called show-through).

It has now been found that, in accordance with the present invention, that certain dyestuffs may be reacted onto the backbone of the aforementioned hot melt ink vehicles, yielding materials which display much improved light stabilities and little tendency for the dye to bleed into the substrate on to which the ink has been printed. These colourants may be used as the majority constituent of a hot melt ink vehicle or simply as a colouring additive to an ink jet ink in which another, colourless, material makes up the majority of the vehicle.

A coloured polymer coating formed by bonding of a reactive colourant to a cross-linking agent which itself is used to cross-link acrylic polymer molecules is disclosed in US-A-5 231 135.

The present invention now provides a coloured material suitable for use in a hot melt ink, the material comprising a oligomeric hot melt ink jet vehicle formed of molecules having a backbone and at least one pendant side-chain, and a dyestuff reacted onto the backbone.

For the avoidance of doubt, in the context of the present invention, the term "dyestuff" includes any substance endowing to the material, a coloured pigmentation within the visible spectrum or any other "optical" property such as UV fluorescence. The words "dyed" and "coloured" are therefore to be interpreted in this light.

Preferably, the coloured material according to the present invention is obtainable as the reaction product of an aliphatic or aromatic mono- or di-isocyanate with a dyestuff which is a hydroxyl group functional component and optionally, one or more other suitable materials. The other suitable materials may be any capable of reacting with the isocyanate groups to form a oligomer, eg. having a urea-linkage, a urethane-linkage.

Such materials include mono- and dihydric alcohols, primary and secondary monoamines, diprimary diamines, functional amides, hydroxy functional amines and hydroxyl containing components having a terminal unsaturated bond.

Suitable functional amides include those which are the reaction products of primary or secondary monoamines, optionally having hydroxyl functionality, or diprimary diamines, and mixtures thereof, together with mono- or difunctional carboxylic acids, also optionally having hydroxyl functionality, and mixtures thereof.

According to one embodiment of the invention, there is provided a material suitable for use as a coloured vehicle in a hot melt ink, and obtainable by reacting an aliphatic or aromatic mono- or di-isocyanate with an at least stoichiometric amount of:

- (i) a hydroxyl group functional dye component;
- (ii) a hydroxyl group functional dye component followed by one or a mixture of monohydric alcohols; or
- (iii) a hydroxyl group functional dye component followed by a dihydric alcohol component followed by a monohydric alcohol component;
- (iv) a hydroxyl group functional dye component followed by one or a mixture of primary or secondary monoamine components;
- (v) a hydroxyl group functional dye component followed by a diprimary diamine component, followed by a primary monoamine component;
- (vi) a hydroxyl group functional dye component, followed by a diprimary diamine component, followed by a monohydric alcohol component;
- (vii) a hydroxyl group functional dye component followed by the reaction product of one equivalent of a primary diamine component with

one equivalent of a monocarboxylic acid and one equivalent of an hydroxy functional monocarboxylic acid;

(viii) a hydroxy group functional dye component, followed by the reaction product of one equivalent of a diprimary diamine component with one equivalent of a monocarboxylic acid;

(ix) a hydroxyl group functional dye component followed by the reaction product of one equivalent of a primary monoamine with hydroxyl group functionality, with one equivalent of monocarboxylic acid;

(x) a hydroxyl group functional dye component followed by the reaction product of (vii) or (viii), but where the acid functionality is made up of a mixture of any two or more of a monocarboxylic acid, a dicarboxylic acid and hydroxy monocarboxylic acids; or

(xi) a hydroxyl group functional dye component followed by a hydroxyl group containing component with terminal unsaturated bonds.

In all cases where the diprimary diamine component is reacted initially with the isocyanate component, it is used in an amount of not more than 50% of the stoichiometric amount of other reactive groups required to react with the isocyanate groups on the diisocyanate. This is not true in the materials which are first reacted with carboxylic acids to form amides.

Very preferably, materials according to the present invention (hereinafter referred to as oligomeric colorants) have a melting point of at least 65°C. This means a melting point as determined by the DSC method. It should be noted that not all of the materials obtainable by the reactions outlined above will have a melting point in excess of 65°C. Experiments have proved that there is a wide range of melting points possible for these materials and that it is extremely difficult to predict, with respect to molecular morphology or weight, what the melting point of a particular material will be. The determination of which materials are suitable therefore has to be left to experiment and trial.

Suitable isocyanates for use in the preparation of the oligomeric colorants include isophorone diisocyanate, toluene diisocyanate, diphenylmethane-4,4'-diisocyanate (MDI), hexamethylene-1,6-diisocyanate, octadecylmonoisocyanate, naphthalene-1,5-diisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, dicyclohexylmethane-4,4'-diisocyanate, trimethylhexamethylene diisocyanate and tetramethylene xylene diisocyanate. Of these diisocyanates, the aliphatic diisocyanates are generally preferred and, in particular isophorone diisocyanate, trimethylene hexamethylene diisocyanate and octadecylmonoisocyanate have been found to give particularly useful oligomeric colorants.

The dyestuffs which have proven useful in this application are those which contain an element of hydroxyl functionality which can form urethane linkages with the isocyanate groups. Such dyes are those in the Reactint urethane colourants range produced by Milliken Chemicals Inc.

A wide variety of monohydric aliphatic alcohols may be used to produce oligomeric colorants of the present invention, e.g. C<sub>1</sub> to C<sub>22</sub> alcohols. Also etherified dihydric alcoholic materials can be utilised, such as propylene glycol methyl ether (PGME), dipropylene glycol methyl ether (DPGME), propylene glycol phenyl ether (PPH) or tripropylene glycol butyl ether (TPGBE). When the monohydric alcohol component is an esterified dihydric alcohol, the esterifying acid may be an ethylenically unsaturated acid such as acrylic or methacrylic acid, thereby introducing ethylenic unsaturation to the oligomeric colorant, rendering it suitable for further cure by UV or electron beam methods once it has been applied to a substrate by hot melt printing. Dihydric alcohols which may be used include ethylene glycol, propylene glycol, polyethylene glycols, polypropylene glycols or 1,6-hexanediol.

Primary and secondary amines which may be used may cover the range between C<sub>1</sub> and C<sub>22</sub> monoamines such as ethylamine, octylamine,

dodecylamine, octadecylamine, hexadecylamine, di-n-butylamine, N-methyloctadecylamine, neopentadamine, di-n-tallow amine and di-n-cocoamine.

Suitable diamines include isophorone diamine, neopentane diamine, hexamethylene diamine, ethylene diamine and polyoxypropylene diamines.

Diamines suitable for the preparation of the hydroxy or amine functional amides are ethylene diamine, neopentane diamine, 2,4,4-trimethylhexanediamine, 2-butyl 2-ethyl 1,5 pentanediamine, 1,3 diaminopentane, isophorone diamine and 2 methyl 1,5 pentamethylene diamene. Hydroxy functional primary and secondary amines which may be used include ethanolamine, diethanolamine and n-methyl ethanolamine.

Monocarboxylic acids which are suitable for this application include stearic acid, acetic acid, 3,5,5 trimethylhexanoic acid, propanoic acid, decanoic acid, 2,2 dimethylpropionic acid, isooctanoic acid, isoheptanoic acid, isobutyric acid or isodecanoic acid.

Hydroxy functional monocarboxylic acids which may be used are 12-hydroxystearic acid, 12-hydroxydodecanoic acid or 2-hydroxyhexanoic acid, 16-hydroxyhexadecanoic acid, 2-hydroxy isobutyric acid. The acid functionality in the reaction may be made up of pure acids or a mixture of any of those mentioned above.

Suitable examples of hydroxyl group containing components with terminal unsaturated bonds include hydroxy ethyl acrylate.

The reaction between the isocyanate and the amine, hydroxy or carboxylic acid groups will proceed without the use of a catalyst. If however, a catalyst is required to facilitate complete reaction of the isocyanate groups, materials such as dibutyl tin dilaurate or stannous octoate can be used.

The average molecular weight of the oligomeric colorants is suitably from 500 to 3000, preferably from 600 to 2000.

For some applications of hot melt inks, it is desirable that the vehicles, the oligomeric colorants, be transparent to light. Again it is virtually impossible to predict whether any particular material will be transparent or not. However, here again it is a matter of simple routine trial and experiment to determine which materials are most suited to the application. Similarly, it is generally desirable that the oligomeric colorants should have relatively low viscosities (e.g. less than 200 centipoise at 125°C) and, here again, it is difficult to make predictions as to the viscosity of any particular oligomeric colorant. Where the oligomeric colorants are used solely as colouring additives, rather than as the major component of the hot melt ink jet ink vehicle, their viscosities may be in excess of 200 centipoise.

The oligomeric colorants of the invention are used as vehicles, or components of the vehicles, of hot melt inks. In addition to the oligomeric colorants, such inks may also contain further colorants, such as dyes or pigments, viscosity adjusting additives and anti-oxidants. Generally the vehicle (oligomeric colorant) will form from 10 to 90% by weight, especially 30-75% by weight of any ink, with viscosity modifying additives making up the bulk of the remainder of the ink and further colorants or antioxidants making up the balance.

The present invention will now be explained in more detail by way of the following non-limiting examples.

#### Example 1

One equivalent of octadecylisocyanate was charged to a reaction flask fitted with a stirrer, a thermometer and a nitrogen sparge line. The flask was heated to 65°C and one equivalent of a hydroxy functional dye, Red X52 (Milliken Chemicals Inc.) was carefully added plus catalyst (dibutyl tin dilaurate), at a rate which ensured that the temperature of reaction did not climb above 100°C. When all of the dye had been added



and all exotherms had ceased, the reaction was heated to 150°C and held at this temperature until the isocyanate content fell below 30 ppm (as determined by titration and IR analysis).

The clear, red coloured solid produced by this reaction had a softening point, as determined by differential scanning calorimetry, of 88°C and a viscosity of 20 centipoise at 125°C.

#### **Example 2**

One mole of trimethylhexamethylene diisocyanate was charged to a reaction flask fitted with a stirrer, thermometer and nitrogen sparge line and warmed to 65°C. To this was added 1.6 moles of octadecanol and 0.4 moles of Yellow X15 reactive dyestuff (Milliken Chemicals Inc.). The dye solution was added slowly, so that the resultant exotherm did not raise the temperature of the reaction above 100°C. When the addition was complete and the batch was no longer exotherming, it was heated to 150°C and held at this temperature until the free isocyanate levels in the vessel had fallen to less than 30 ppm. The batch was then discharged to yield an opaque yellow solid with a DSC softening point of 52 °C, and a viscosity of 25 centipoise at 125°C.

#### **Example 3**

One mole of trimethylhexamethylene diisocyanate was charged to a flask and heated to 60°C with stirring and under an inert atmosphere of nitrogen. Octadecylamine, 1.62 moles, was then drip fed into the flask so that the reaction temperature did not climb above 100°C. When all the amine had been added, 0.38 moles of reactive dyestuff, Blue 17AB (Milliken Chemicals Inc.) and catalyst were slowly added, again at a rate to keep the reaction temperature below 100°C. When the reaction stopped exotherming, it was heated to 150°C and held there until the free isocyanate content had dropped below 30 ppm.

This reaction produced a transparent blue solid, with a DSC softening point of 80°C, and a viscosity of 210 centipoise at 125°C.

#### Example 4

One mole of trimethylhexamethylene diisocyanate was charged to a flask and heated to 65°C with stirring and under an inert atmosphere of nitrogen. Then 1 mole of a reactive dyestuff Violet X80LT was added with catalyst and the temperature raised to 120°C. After this reaction had reached completion the batch temperature was reduced to 100°C. Hydroxyethyl acrylate, 1 moles was then carefully added along with inhibitor (Ethanox 703) to the reaction flask, keeping the resultant exotherm to below 130°C until the free isocyanate value of the resulting compounds was < 30 ppm.

This reaction yielded a violet coloured, transparent liquid with a viscosity of 16.4 poise at 75°C.

#### Example 5

A hydroxy functional diamide material was prepared by reacting one mole of ethylene diamine with 1.0 moles of 3,5,5-trimethylhexanoic acid and 1.0 moles of 12-hydroxystearic acid.

One mole of trimethyl hexamethylene diisocyanate was charged to a reaction flask and heated under stirring and nitrogen to 65°C. 1.0 mole of the diamide material produced by the reaction above was powdered and slowly fed into the isocyanate, so that the reaction temperature did not rise above 100°C. When all the diamide was added and the exotherm had abated, reactive dye Red X52 (Milliken Chemicals Inc.) (1.0 moles) and catalyst (dibutyl tin dilaurate) was fed into the reaction in a similar way. When all exotherming had ceased the batch was heated to 155°C and maintained at this temperature until the level of unreacted isocyanate groups had fallen below 30 ppm.

The transparent red solid material produced had a DSC softening point of 88°C, and a viscosity of 600 centipoise at 125°C.

## CLAIMS

1. A coloured material suitable for use in a hot melt ink, the material comprising a oligomeric hot melt ink jet vehicle formed of molecules having a backbone and at least one pendant side-chain and a dyestuff reacted onto the backbone.
2. A material according to claim 1, obtainable as the reaction product of an aliphatic or aromatic mono- or di-isocyanate with a dyestuff which is a hydroxyl group functional dye component and optionally, one or more other suitable materials.
3. A material according to claim 1 or claim 2, formed as a reaction product of the isocyanate and hydroxyl group functional dye component together with at least one suitable material selected from mono- and dihydric alcohols, primary and secondary monoamines, diprimary diamines, functional amides, hydroxyl functional amines and hydroxyl containing components having a terminal unsaturated bond.
4. A material according to claim 3, formed as a reaction product including at least one functional amide selected from those which are the reaction products of primary or secondary monoamines, optionally having hydroxyl functionality, or diprimary diamines, and mixtures thereof, and mono- or difunctional carboxylic acids, also optionally having hydroxyl functionality, and mixtures thereof.

5. A material according to any preceding claim, obtainable by reacting an aliphatic or aromatic mono- or di-isocyanate with an at least stoichiometric amount of:

- (i) a hydroxyl group functional dye component;
- (ii) a hydroxyl group functional dye component followed by one or a mixture of monohydric alcohols; or
- (iii) a hydroxyl group functional dye component followed by a dihydric alcohol component followed by a monohydric alcohol component;
- (iv) a hydroxyl group functional dye component followed by one or a mixture of primary or secondary monoamine components;
- (v) a hydroxyl group functional dye component followed by a diprimary diamine component, followed by a primary monoamine component;
- (vi) a hydroxyl group functional dye component, followed by a diprimary diamine component, followed by a monohydric alcohol component;
- (vii) a hydroxyl group functional dye component followed by the reaction product of one equivalent of a primary diamine component with one equivalent of a monocarboxylic acid and one equivalent of a hydroxy functional monocarboxylic acid;
- (viii) a hydroxy functional dye component, followed by the reaction product of one equivalent of a diprimary diamine component with one equivalent of a monocarboxylic acid;
- (ix) a hydroxyl group functional dye component followed by the reaction product of one equivalent of a primary monoamine with hydroxyl group functionality, with one equivalent of monocarboxylic acid;
- (x) a hydroxyl group functional dye component followed by the reaction product of (vii) or (viii), but where the acid functionality is made

up of a mixture of any two or more of a monocarboxylic acid, a dicarboxylic acid and hydroxy monocarboxylic acids; or

(xi) a hydroxyl group functional dye component followed by a hydroxyl group containing component with terminal unsaturated bonds.

6. A material according to any preceding claim, having a melting point of at least 65°C.

7. A material according to any one of claims 2-4, wherein the isocyanate is selected from isophorone diisocyanate, toluene diisocyanate, diphenylmethane-4,4'-diisocyanate (MDI), hexamethylene-1,6-diisocyanate, octadecylmonoisocyanate, naphthalene-1,5-diisocyanate, 3,3'-dimethyl-4,4'-biphenyldiisocyanate, dicyclohexylmethane-4,4'-diisocyanate, trimethylhexamethylene diisocyanate and tetramethylene xylene diisocyanate.

8. A material according to any of claims 3-5, obtainable from reactants which include at least one monohydric aliphatic alcohol selected from C<sub>1</sub> to C<sub>22</sub> alcohols.

9. A material according to any of claims 3-5, obtainable from reactants which include at least one etherified dihydric alcoholic material selected from propylene glycol methyl ether (PGME), dipropylene glycol methyl ether (DPGME), propylene glycol phenyl ether (PPH) and tripropylene glycol butyl ether (TPGBE).

10. A material according to any one of claims 3-5, obtainable from reactants which include at least one monohydric esterified dihydric alcohol

component in which, the esterifying acid is an ethylenically acrylic or methacrylic acid.

11. A material according to any one of claims 3-5, obtainable from reactants which include at least one dihydric alcohol selected from ethylene glycol, propylene glycol, polyethylene glycols, polypropylene glycols and 1,6-hexanediol.
12. A material according to any of claims 3-5, obtainable from reactants which include at least one primary or secondary C<sub>1</sub> - C<sub>22</sub> monoamine selected from ethylamine, octylamine, dodecylamine, octadecylamine, hexadecylamine, di-n-butylamine, neopentadamine, N-methyl octadecylamine, di-n-tallow amine and di-n-cocoamine.
13. A material according to any one of claims 3-5, obtainable from reactants which include at least one diprimary diamine selected from isophorone diamine, neopentane diamine, hexamethylene diamine, ethylene diamine and polyoxypropylene diamines.
14. A material according to claim 3 or claim 4, obtainable from reactants which include at least one functional amide obtainable as the reaction product of at least one diamine selected from ethylene diamine, neopentane diamine, 2,4,4-trimethylhexanediamine, isophorone diamine, 2-butyl 2-ethyl 1,5, pentanediamine, 1,3 diaminopentane and 2 methyl 1,5 pentamethylene diamene.
15. A material according to claim 3 or claim 4, obtainable as the reaction product of at least one hydroxy functional amine selected from ethanolamine, diethanolamine and n-methyl ethanolamine.

16. A material according to any of claims 3-5, obtainable from reactants which include at least one monocarboxylic acid selected from stearic acid, acetic acid, propanoic acid, 3,5,5 trimethylhexanoic acid, decanoic acid, 2,2 dimethylpropionic acid, isooctanoic acid, isoheptanoic acid, isobutyric acid or isodecanoic acid.
17. A material according to any of claims 3-5, obtainable from reactants which include at least one hydroxy functional monocarboxylic acid selected from hydroxystearic acid, 16-hydroxyhexadecanoic acid, 2-hydroxyisobutyric acid, 12-hydroxydodecanoic acid or 2-hydroxyhexanoic acid.
18. A material according to any of claims 3-5, obtainable from reactants which include at least one hydroxyl group containing component having a terminal unsaturated bond which is hydroxy ethyl acrylate.
19. A material according to any preceding claim, having an average molecular weight from 500 to 3000, preferably from 600 to 2000.
20. A material according to any preceding claim, having a viscosity in excess of 200 centipoise at 125°C.
21. A hot melt ink comprising a material according to any preceding claim.
22. A hot melt ink according to claim 21, wherein the said material forms from 30 to 75% by weight of the total ink composition.



23. A coloured material suitable for use in a hot melt ink, the material being substantially as hereinbefore described with reference to any of the examples.

<p style="text-align: center;">17</p> <p><b>Patents Act 1977</b>  <b>Examiner's report to the Comptroller under Section 17</b>  <b>(The Search report)</b></p>		<p>Application number  GB 9520470.7</p>
<p><b>Relevant Technical Fields</b></p> <p>(i) UK Cl (Ed.N)      C3R RSM, RSX, RJ; C3P PDA  (ii) Int Cl (Ed.6)      C09B 69/10; C09D 11/00C4</p>		<p>Search Examiner  ALAN KERRY</p>
<p><b>Databases (see below)</b>  (i) UK Patent Office collections of GB, EP, WO and US patent specifications.</p>		<p>Date of completion of Search  29 DECEMBER 1995</p>
<p>(ii) ONLINE DATABASE: WPI</p>		<p>Documents considered relevant following a search in respect of Claims :-  1-23</p>

**Categories of documents**

<b>X:</b>	Document indicating lack of novelty or of inventive step.	<b>P:</b>	Document published on or after the declared priority date but before the filing date of the present application.
<b>Y:</b>	Document indicating lack of inventive step if combined with one or more other documents of the same category.	<b>E:</b>	Patent document published on or after, but with priority date earlier than, the filing date of the present application.
<b>A:</b>	Document indicating technological background and/or state of the art.	<b>&amp;:</b>	Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages		Relevant to claim(s)
X	GB 2038849 A	(PCUK) see Claims 1-7; Examples 1-19	1-3, 5 at least
X	US 5264507 A	(BASF) see Claim 1; Table II, Examples 5, 14	1 at least
X	US 5098475 A	(XEROX) see Claim 1; Examples I-IV	1 at least
X	EP 0540248 A2	(HEWLETT PACKARD) see Claims 1, 8, 10	1 at least

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